Photochemical Alkyl Nitrate Production

For two daughter alkyl nitrates a and b that originate from the same parent hydrocarbon ($\geq C_5$) [Flocke et al., 1998]:

$$\frac{[\mathsf{RONO}_2]_a}{[\mathsf{RONO}_2]_b} = \frac{(\alpha_1 \alpha_2)_a}{(\alpha_1 \alpha_2)_b}$$

- ❖ [RONO₂]_a / [RONO₂]_b: TRACE-P msts.
- α₁, α₂: Atkinson [1987]
 Atkinson et al. [1987]
 Kwok and Atkinson [1995]
 Arey et al. [2001]

Alkyl Nitrate Evolution

 $RH + OH \rightarrow R + H_2O$ For: k_1

 $RONO_2 + OH \rightarrow products$ k_2

 $RONO_2 + hv \rightarrow RO + NO_2$ J_{RONO2}

 $k_{\mathsf{A}} = k_1 [\mathsf{OH}]$ where:

 $k_{\rm B} = k_2 \left[{\rm OH} \right] + J_{\rm RONO2}$

Evolution of alkyl nitrates in an air mass [Bertman et al., 1995]:

$$\frac{[RONO_2]}{[RH]} = \frac{\alpha_1 \alpha_2 k_A}{(k_B - k_A)} \left(1 - e^{(k_A - k_B)t}\right)$$

TRACE-P msts. α_1 , α_2 : *Atkinson* [1987] Atkinson et al. [1987] Kwok and Atkinson [1995] Arey et al. [2001]

 J_{RONO2} : J. Crawford [pers. comm.]

[OH]: from the Eisele group

Conclusions

- 1. **7 C₁-C₅ alkyl nitrates** measured in whole air samples during TRACE-P (DC-8 & P3-B)
- anticipate 2 alkyl nitrate papers:
 distribution; (2) kinetics
- 3. **photochemical cn. marine** alkyl nitrate production evident
- 4. **production and evolution** curves using **field** measurements are being compared with predicted curves using **laboratory** kinetic data



